Predicting and Evaluating the Effectiveness of Ocean **Carbon Sequestration by Direct Injection**

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Predicting and evaluating the effectiveness of ocean carbon sequestration by direct injection

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Abstract

Direct injection of CO, into the ocean is a potentially effective carbon sequestration strategy. Therefore, we want to understand the effectiveness of oceanic injection and develop the appropriate analytic framework to allow us to compare the effectiveness of this strategy with other carbon management options. Here, after a brief review of direct oceanic injection, we estimate the effectiveness of ocean carbon sequestration using one dimensional and three dimensional ocean models. We discuss a new measure of effectiveness of carbon sequestration in a leaky reservoir, which we denote sequestration potential. The sequestration potential is the fraction of global warming cost avoided by sequestration in a reservoir. We show how these measures apply to permanent sequestration and sequestration in leaky reservoirs, such as the oceans, terrestrial biosphere, and some geologic formations. Under the assumptions of a constant cost of carbon emission and a 4 % discount rate, injecting 900 m deep in the ocean avoids ~90 % of the global warming cost associated with atmospheric emission; an injection 1700 m deep would avoid > 99 % of the global warming cost. Hence, for discount rates in the range commonly used by commercial enterprises, oceanic direct injection may be nearly as economically effective as permanent sequestration at avoiding global warming costs.

Introduction

Our society needs to understand the options available for controlling levels of atmospheric carbon dioxide, should the threat of CO₂-induced harmful climate change prove real. If we wait until there is definitive proof of harmful climate change, it will be too late to develop large-scale solutions to the problem [Hoffert et al., 1998].

The oceans contain approximately 50-fold more carbon than the atmosphere and already play an

important role in the storage of fossilfuel carbon. About one-third of the carbon dioxide we emit (2 of 6 PgC/yr) is being absorbed by ocean surface waters and mixed to the deep ocean, with unknown long-term effects.

There are two major proposed strategies for ocean carbon sequestration:

 deliver CO₂ to deep waters by direct injection (avoiding climate effects and the biologically rich surface layer); increase the flux of organic carbon sinking to the deep waters by stimulating the natural biological pump in the surface ocean with the addition of nutrients.

Both strategies raise issues regarding environmental impacts, feasibility, and effectiveness. Sequestration strategies must not, in the long run, cause more environmental problems than they solve. Viable strategies must present tractable engineering problems and be able to make a real contribution to slowing the accumulation of CO₂ in the atmosphere.

CO₂ injection into the deep and intermediate ocean must be environmentally acceptable to the public at large. Even if the evidence indicates low risk, the public will need clear, complete information to understand its implications.

Review of studies on direct carbon injection

Direct injection of CO₂ into the ocean interior has been proposed as approach to slow the growth atmospheric carbon dioxide content [Herzog et al., in press]. The direct carbon injection concept was first mentioned by Marchetti [1977] who conceived of piping CO₂ into the outflow of the Mediterranean Sea, where it would sink deeper into the Atlantic. The idea of this approach is to inject fossil-fuel carbon dioxide into the ocean interior, thereby bypassing the slow mixing processes that would otherwise inhibit the transfer of excess atmospheric CO₂ into the ocean interior. For a specified energy demand scenario, direct injection of CO₂ in the ocean could slow CO₂ accumulation in the atmosphere, and thus global warming. However, this

would be at the expense of higher atmospheric CO₂ content in the distant future, due to the energy costs of injection [Kheshgi *et al.*, 1994].

Several methods for the direct injection of CO_2 into the ocean have been proposed:

- injecting liquid CO₂ at a depth of ~1000 m from a manifold lying near the ocean bottom and forming a rising droplet plume [Liro et al., 1992];
- (2) injecting liquid CO₂ at a depth of > 3000 m from a manifold near the ocean bottom and forming a sinking droplet plume;
- (3) creating a dense CO₂-seawater mixture at a depth of between 500 and 1000 m forming a sinking bottom gravity current [Haugan and Drange, 1992];
- (4) releasing dry ice at the ocean surface from a ship [Nakashiki et al., 1991];
- (5) injecting liquid CO₂ at a depth of about 1000 m from a pipe towed by a moving ship and forming a rising droplet plume [Ozaki *et al.*, 1995];
- (6) introducing liquid CO₂ to a sea floor depression forming a stable "deep lake" at a depth of about 4000 m [Ohsumi, 1995].

The evaluation of each scenario involves issues of environmental impact, sequestration efficiency, cost, and technical feasibility [Herzog *et al.*, 1995]. Options (1), (2), (5), and (6) have received most recent attention.

Review of biotic impacts

The consequences of increasing CO₂ concentrations for marine biota are poorly understood. Work to try to fill in these gaps has begun at Monterey Bay Aquarium Research Institute (MBARI) [e.g., Tamburri *et al.*, 2000] and at other locations.

It has been widely recognized that the greatest impact from deep-sea CO2 injection is likely to be a result of the change in deep-sea pH [Magnesen and Wahl, 1993]. It is important to note that the ocean is naturally sequestering anthropogenic carbon dioxide, and as the fossil-fuel reserves are burned, deep-sea pH is expected to decrease by as much as 0.5 pH units [Herzog et al., 1995]. Magnesen and Wahl [1993] estimate that changes in ocean pH of more than 0.2 units will have some detectable biological impact. Rau and Caldeira [1999] and Caldeira and Rau [2000] have proposed using the dissolution of carbonate minerals to minimize the pH effects of adding CO₂ to the ocean.

Perhaps the most extensive modeling of the biological impacts of deep-sea CO₂ injection has been performed by the MIT Energy Laboratory [Caulfield, 1996; Adams and Herzog, 1996; Caulfield et al. 1997; Adams et al., 1997]. These biological impacts are likely to be greatest in the near field, near the point of emission, but lesser impacts over a broader region of the ocean are also to be expected. Based on a number of authors biological studies, these developed an estimate of the mortality of marine organisms subjected to an exposure to low-pH waters for a specified amount of time. For a droplet plume scenario, these authors concluded that a typical power plant would produce on the order of 1 km³ of water with pH

< 7. At this pH, many marine organisms may be relatively unaffected, but some species begin to show some signs of mortality. Nematodes and bacteria show drastic impacts only for pH less than 5.5 or 6 or less [Takeuchi et al., 1997]. The volume of water with pH < 7 scales nonlinearly with the amount of CO₂ emitted, such that diffuse and widely dispersed CO₂ emitters will minimize mortality. Because diapycnal diffusivity is far less efficient a transport mechanism than isopycnal diffusivity, expanding the vertical spacing of emission would likely be less expensive and more effective than increasing spacing in the horizontal direction.

Golomb et al. [1992] suggested that other impacts of deep-sea CO2 disposal could include interference with feeding patterns of swimming creatures and burial of benthic organisms by CO₂hydrate on the sea floor. Golomb [1993] suggests that far-field effects of deep-sea injection are likely to be negligible. hardware, the injection Around ecosystems with enhanced biological activity are likely to form, such as those found around oil drilling platforms. It is less clear how marine organisms will respond to a stream of rising CO₂ droplets, however, marine biota have not shown great interest in rising CO2 observed during in-situ droplets Brewer, experiments ſP. personal communication, 1999]. Low pH could have direct effects on cell membranes or could cause conditions that will tend to erode calcareous components of marine organisms [Golomb, 1993].

Shirayama [1998] suggests that the long life span, low biological activity, high sensitivity to environmental disturbance, high species diversity, and low density of deep-sea organisms make them potentially vulnerable to rather modest changes in ocean chemistry in ways that may be as yet unforeseen. Shirayama suggests that long-term in situ experiments can help us to develop a better understanding of the far-field biological and geochemical consequences of adding carbon to the ocean.

Review of direct CO₂ injection simulations

Model simulations are used to estimate the effectiveness of direct CO, injection into the ocean (Figure 1). The largescale effectiveness of direct CO₂ injection was first simulated by Hoffert et al. [1979]. Since that time, there have been several model-based studies of deep-injection of carbon dioxide using schematic ocean models [Flannery et al., 1993; Kheshgi et al., 1994; Cole et al. 1993; Wong and Mattear, 1993] and global ocean general circulation models [Xu et al., 1999; Nakashiki and Ohsumi, 1997; Dewey et al., 1997; Bacastow et al., 1997; Stegen et al., 1993]. These studies have indicated that deep injection of carbon dioxide could be an effective means of sequestering CO₂ in the oceans for hundreds of years or more.

In a comparison of simulated CO₂ injection near Tokyo and New York City, the model of Dewey et al. [1997] found that injection off New York would be more effective than injection off Tokyo; however, results at LLNL (Figure 2) and from other groups [J. Orr, personal communication, 1999] indicate the reverse. The fact that the results of these models are contradictory indicates the need for improved model development and evaluation, and performing simulations in a variety of models.

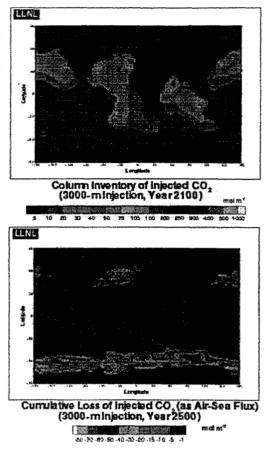


Figure 1. Simulation of direct CO₂ injection at seven locations at 3000 m depth. Over 75 % of the carbon is retained over 500 years. Most of the leakage to that atmosphere occurs in the Southern Ocean and in the North Atlantic, where the cold dense waters of the deep ocean contact the atmosphere. (Simulations were performed at LLNL for DOCS under OCMIP protocols.)

The effectiveness of CO₂ disposal is affected by both transport and chemical considerations. Wong and Mattear [1993] find that the effectiveness of CO₂ injection off the coast of Japan would be somewhat limited by the low carbonateion concentrations of North Pacific waters. In other basins, interactions between injected CO₂ and carbonate sediments could significantly increase the effectiveness of deep-sea CO₂

injection [De Baar, 1992; Wilson, 1992; Cole *et al.*, 1993].

are trade-offs between There effectiveness maximizing and minimizing biological impacts of direct injection. Isopycnal (nearly horizontal) dispersion is many millions of times more efficient that diapycnal (nearly dispersion; thus, enhancing vertical) dispersion is critical vertical minimizing pH impacts both in the near field and in the far field. Thorkildsen and Alendal [1997] modeled the near-field dynamics of a 1-cm-diameter CO₂ droplet in sea-water at 1 km depth. In this range the CO₂ is less dense than the surrounding seawater, and they found that the buoyant rise of the liquid CO₂, followed by the sinking of the CO₂-laden seawater led to the dispersal of the CO₂ over a vertical range of 250 m. Morishita et al. [1993] found that the results of such calculations are sensitive to the rate of CO₂ dissolution, which in turn depends on droplet size. Droplet size can be manipulated [Teng et al., 1997] to optimize the trade-off between increased dispersion of the CO₂ near the plume source and decreased mean depth, and hence effectiveness, of CO₂ injection. Hirai et al. [1997] found that the formation of clathrates on the CO₂ droplet surface impeded dissolution of the released CO₂, which could increase dispersion of released CO₂. Brewer et al. [1999, 2000] have been conducting in situ experiments with submersibles to provide the basic data on which CO₂ droplet dissolution models can be based.

It has been suggested that the effectiveness of deep-sea disposal would be increased if the CO₂ formed clathrates and/or a clathrate-covered CO₂ lake on the seafloor [e.g., Nakashiki, 1997; Spencer and North, 1997]. Ohsumi *et al.*

[1992] have modeled the behavior of a CO, lake on the sea floor, based on a set of laboratory experiments of CO₂ properties under relevant conditions. They found that it was important to take into consideration the increase in density of the overlying seawater and assumed that the rate of dissolution of the "lake" would be controlled by transport of carbon in the overlying boundary layer. Observations reported by Nakashiki also indicate that bottom [1997] boundary layer processes would control dissolution of a CO2 lake.

Estimating the effectiveness of direct injection

In this next section, we estimate the effectiveness of ocean sequestration as a function of depth of injection. We performed a set of simulations of direct injection of CO₂ into the ocean using both a one dimensional box-diffusion model [Caldeira et al., 1998] and in a three dimensional global general circulation model [Caldeira and Duffy, 2000].

One dimensional ocean model.

For the one dimensional model, we represented the ocean by a box-diffusion al., 1975; Oeschger etmodel Siegenthaler, 1983] with a 75 m thick mixed-layer and a total depth of 3800 m, as described by Caldeira et al. [1998]. Ocean carbon chemistry [Stumm and Morgan, 1981] is calculated using a surface temperature of 18 °C, salinity of 35 psu, and alkalinity of 2.23 eq m⁻³, with constants as specified in Roy et al. [1993], Dickson [1990], Millero [1995], and Weiss [1974]. The eddy diffusion and gas-transfer velocity coefficients were chosen such that the change in ocean ¹⁴CO₂ inventory between 1945 and

1975 matches the estimated 1975 bomb radiocarbon inventory [Broecker et al., 1995] of 305 x 10^{26} atoms, and the modeled 1975 ocean mean and surface ocean Δ¹⁴CO₂ matches the basin-volumeweighted mean of the natural plus bomb $\Delta^{14}CO_2$ values measured in GEOSECS program [Broecker et al., 1985]. This tuning yielded a vertical eddy diffusion coefficient is 8,820 m² yr⁻¹ at the base of the mixed-layer, diminishing with an e-folding length scale of 500 m to a minimum of 2,910 m² yr⁻¹ at the ocean bottom. The tuned gas transfer velocity is equivalent to 0.0543 mol m⁻² µatm⁻¹ yr⁻¹ at 18 °C. In this model, the state variables are ¹²C, ¹³C, and ¹⁴C masses or concentrations, not ratios or normalized ratios such as Δ^{14} C or δ^{13} C. Throughout, fractionation factors for 14C are assumed to be the square of the ¹³C fractionation factor. and all fractionation factors are from Tans et al. [1993]. Because ¹³C and ¹⁴C compose a very small fraction of the total C atoms, we use 12C mass and fluxes interchangeable with C mass and fluxes.

Three dimensional ocean model.

For the three dimensional simulations, we used the same configuration of the LLNL ocean general circulation model as described in more detail in Caldeira and Duffy [2000]. The LLNL ocean general circulation model is based on the GFDL Modular Ocean Model (MOM) [Pacanowski et al., 1991], with the addition of the Gent-McWilliams parameterization [Gent and McWilliams, 1990] of transport of tracers by subgrid scale eddies and coupling to the dynamic/thermodynamic sea ice model of Oberhuber [1993]. Our model uses a mesh of 2 degrees (latitude) by 4 degrees (longitude) with 23 vertical levels. The model was tuned to approximately simulate the Δ^{14} C values observed in the deep central North Pacific ocean. The model results shown here represent the model configuration that is LLNL's entry in the Ocean Carbon-cycle Model Intercomparison Project (OCMIP; http://www.ipsl.jussieu.fr/OCMIP).

Model simulations

Both the one and three dimensional models were run under the sequestration scenarios described in the OCMIP sequestration protocols described at http://www.ipsl.jussieu.fr/OCMIP. atmospheric CO₂ concentration was specified to be the IPCC S650 scenario, and injection was performed at 7 different locations at 3 different depths at a rate of 0.1 PgC/yr for 100 years starting in year 2000 and continuing another 400 years with no injection. This S650 protocol is conservative in that injected CO2 that leaks out to the atmosphere is not permitted to re-enter the ocean, as it would in the real world discussion below). Injection locations are near: (1) the Bay of Biscay, (2) New York City, (3) Rio de Janeiro, (4) San Francisco, (5) Tokyo, (6) Jakarta, and (7) Bombay.

Model results

The basic results for the model simulations are presented in Table 1 and Figure 2. The figure represents the amount of the injected carbon remaining in the ocean as a function of time for all of the injection locations, as well as for the one dimensional model. With perfect retention the lines would slope up at 0.1 PgC yr⁻¹ until year 100 and then remain at 10 PgC thereafter. Injection at 3000 m is quite effective at sequestering carbon from the atmosphere for several

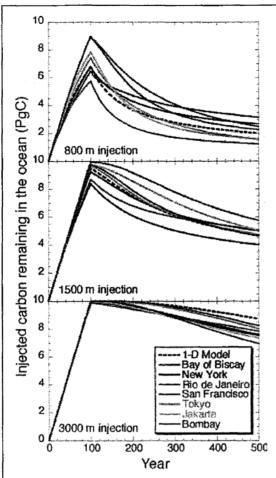


Figure 2. Comparison of one-dimensional and three-dimensional model results for injections as described under OCMIP protocols. The top, middle, and bottom panels show results for injections at 800 m, 1500 m, and 3000 m depth, respectively. For exploring basic conceptual issues, a one-dimensional model adequately represents the behavior of the three-dimensional model.

centuries, whereas injection at shallower depths is less effective. In general, injections into the Pacific Ocean are more effective than injection at the same depth in the Atlantic Ocean.

The one dimensional box-diffusion model represents the behavior of the three dimensional model quite well at 800 m and 1500 m, but the model somewhat overpredicts retention at the

Table 1. CO₂ retention at 500 years.

	Box-	Ocean
	diffusion	GCM
	model	
Depth of	500-year	Mean 500
injection	retention	year
		retention
		± 1 S.D.
800 m	20 %	21 ± 7 %
1500 m	46 %	49 ± 5 %
3000 m	87 %	76 ± 4 %

Table 1. CO_2 remaining at 500 years. Comparison of retention of CO_2 injected into the ocean at three different depths using a one-dimensional box-diffusion model and a three-dimensional ocean GCM. Especially at shallower depths, the 1-D model results accord well with 3-D model results, indicating that the 1-D model is an appropriate tool for exploring basic conceptual issues associated with direct CO_2 injection into the ocean.

3000 km depth. This difference at depth is due to the fact that the one dimensional model lacks an advective pathway to more rapidly bring carbon from the deep ocean to the ocean surface.

Deeper injection is associated with increased retention in both models. In the 3-D model, the standard deviation of the retention across the seven injection locations is small compared to the difference in mean retention across the three injection depths. This suggests that depth of injection is the major control on retention efficiency for injected carbon dioxide.

We conclude that for studies of fundamental issues in direct ocean CO₂ injection, a one dimensional model provides a reasonable prediction. Of course, comparison of different potential sites or an examination of biotic impacts

would require site-specific three dimensional modeling.

Accounting for a leaky ocean

Occasionally, we hear claims that > 80 % of the carbon injected in the ocean will remain in the ocean. Then, in other contexts we hear that all the CO_2 leaks out on a time scale of 300 years for some injection locations. How can these superficially differing claims be reconciled?

A leaky geologic reservoir

To clear up confusion, we will discuss leakage of CO₂ from a geologic reservoir and then draw parallels between this discussion and leakage of CO₂ from the ocean.

If CO₂ were injected into a leaky geologic reservoir, this would be equivalent to a slow flux of CO2 to the atmosphere over an extended period of time. If a system of carbon-trading credits were in place, one of several reasonable approaches to account for this CO₂ flux would be to charge for the CO₂ as it enters the atmosphere. Some of this leaking CO₂ will enter the ocean through the natural processes by which the ocean takes up anthropogenic CO₂. If we were to ask the question, how much carbon is sequestered at a given time by CO₂ injection to the leaky reservoir, the answer would be: the amount of CO₂ remaining in the geologic reservoir. We would not add on to this the amount of carbon that has fluxed through the atmosphere to the ocean.

A leaky oceanic reservoir

The situation with ocean carbon sequestration is less clear because CO₂ degasses from the ocean to the

atmosphere and is reabsorbed by the ocean. How should this be accounted for?

In judging the effectiveness of the leaky geologic sequestration case, we did not consider the flux that would have been driven into the ocean by CO₂ leaked to the atmosphere. Similarly, when judging the effectiveness of ocean carbon sequestration, we should not consider the reabsorption of CO₂ that has degassed to the atmosphere.

accomplished This can be by considering the atmospheric boundary conditions under which a computer model could be run to estimate sequestration effectiveness for a given amount of CO₂ deposited in the ocean at some discrete time. The model could be run with a prescribed atmospheric CO₂ concentration, or it could be run with an atmospheric CO₂ concentration that increases as the sequestered CO₂ outgasses.

Under the fixed-atmospheric CO₂ boundary condition, all of the injected CO₂ will have leaked back to the atmosphere in the steady state. Under the responsive atmospheric CO₂ boundary condition, around 80 % of the injected CO₂ remains in the ocean in the steady state.

We suggest that the fixed atmospheric CO_2 boundary condition is the appropriate one for measuring the effectiveness of ocean sequestration strategies. With this boundary condition, we do not take credit for the natural uptake of excess CO_2 from the atmosphere.

To illustrate some of these issues we present some results from the one dimensional box-diffusion model described above. Figure 3 shows the

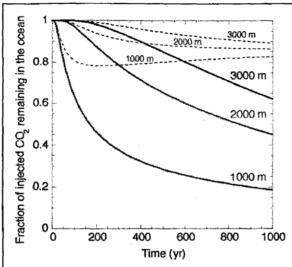


Figure 3. Fraction of injected CO₂ remaining in the ocean at three different depths as predicted by the one-dimensional model described in the text. Solid lines represent the fixed atmospheric CO₂ boundary condition. Dashed lines represent the responsive atmospheric CO₂ boundary condition. The solid lines represent the appropriate amount of carbon to attribute to purposeful carbon sequestration.

results of the model for amount of carbon remaining in the ocean as a function of time, for the cases in which atmospheric CO₂ content both does and does not respond to leakage from the ocean, from a base state of 280 ppm. Figure 4 shows the corresponding fluxes of CO₂ to the atmosphere.

Analytic framework with a worked example

How do we compare the benefits of storing CO₂ in a leaky reservoir with, say, atmospheric release or permanent sequestration? Here, we develop a mathematical formalism to permit such comparison. Our formalism is based on the concepts of

global warming cost, GWC, the net present value of the costs associated

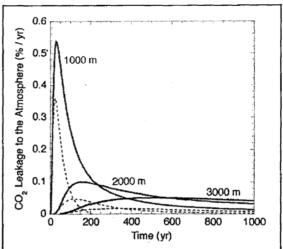


Figure 4. Fluxes of carbon to the atmosphere for the injection scenarios represented in Fig. 3. A 0.1 on the vertical axis means that 0.1 % of the initially injected CO₂ leaks back to the atmosphere during a given year. Notice that leakage of injected carbon to the atmosphere starts off at zero, and then increases to some maximum before diminishing towards zero. Ocean sequestration moves carbon emissions from the present to the future, potentially to economic benefit, due to the role of discounting in reducing the present value of costs incurred in the distant future.

with a time-history of emissions of greenhouse gases, and

sequestration potential, SP, the fraction of global warming costs avoided by sequestering carbon in a reservoir, relative to the cost of immediate atmospheric release.

Let us suppose that the cost of carbon released to the atmosphere is C(t), where this cost may vary as a function of time, t. Depending on the application, C(t) may represent CO_2 taxes, cost of CO_2 credits, direct and indirect environmental costs, or other relevant measures associated with release of CO_2 to the atmosphere.

Net present value is a convenient tool for evaluating carbon sequestration options [Reilly, 2001]. Let us suppose the

reservoir leaks at a rate, L(t). Then, the global warming cost, GWC, for a real discount rate of i, would be the net present value of the cost of emissions from the leaky reservoir:

$$GWC = \int_{t=0}^{\infty} \frac{C(t)L(t)}{(1+i)^{t}} dt .$$
 (1)

Let us suppose a reservoir leaks at a rate proportional to the amount of CO_2 remaining in the reservoir. If the residence time of CO_2 in the reservoir is some time, τ , then for an initial storage of M moles of carbon the leakage can be described by

$$L(t) = \left(\frac{M}{\tau}\right) e^{-t/\tau} . \tag{2}$$

We note that equation (2) is not an accurate representation of leakage from the ocean, but is used here as a simple example. Equation (2) starts off with a maximum leakage immediately after a CO₂ injection, whereas oceanic injection starts off with near-zero leakage, with the leakage increasing to some maximum and then diminishing (Figure 4).

If, for simplicity, we assume the cost, C(t), remains constant with time at some value, C_0 , then substituting equation (2) into equation (1) and integrating, we have that the global warming cost of emissions from an idealized leaky reservoir would be

$$GWC = \frac{M \cdot C_0}{1 + \tau \cdot Ln[1 + i]} . \tag{3}$$

The global warming cost for permanent sequestration $(\tau = \infty)$ is zero. The global warming cost of immediate emission to the atmosphere $(\tau = 0)$ would be the mass of the emission, M, times the cost of emission per unit mass, C_0 ,

Table 2. Symbols used in the text			
Variable	Units	Description	
t	yr	Time after CO ₂ is injected into the reservoir	
τ	yr¹	Residence time of CO ₂ in the sequestration reservoir	
М	Mol C	Molar mass of carbon	
L(t)	Mol C yr ⁻¹	Rate of CO ₂ leakage from the reservoir	
C(t)	\$ (Mol C) ⁻¹	Cost per mol C released to the atmosphere	
i	yr-1	Real economic discount rate	
SP		Fraction of global warming costs, GWC, avoided, due to sequestration in a reservoir	
GWC	\$	Present-value of the cost associated with a time series of CO ₂ emissions	
GWC _e	\$	The cost associated with a CO ₂ emission	

$$GWC_e = M \cdot C_0 . \tag{4}$$

We define the sequestration potential to be the avoided discounted global warming cost achieved by sequestering CO_2 in a reservoir, divided by the discounted global warming cost of atmospheric emission of that CO_2 .

$$SP = \frac{GWC_e - GWC}{GWC_e} \ . \tag{5}$$

The sequestration potential, SP, takes on the value of one for permanent sequestration, and zero for immediate atmospheric release.

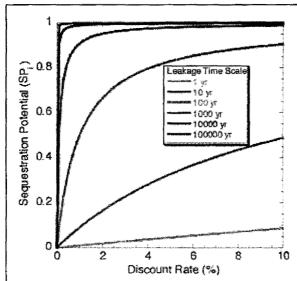


Figure 5. Sequestration potential for an idealized leaky reservoir as a function of discount rate for a variety of residence times (τ). For a discount rate of 5 % per year, sequestering CO_2 in a reservoir that leaks on the time scale of 100 yr saves approximately 80 % of the global warming cost of the CO_2 . For this discount rate, a reservoir that leaked on the 1000 yr time scale would save ~98 % of the global warming cost. Curves are calculated from equation (6).

In our simplified example (i.e., constant CO_2 emissions cost, reservoir leaks with a single exponential time scale) the sequestration potential, SP, can be found analytically as a function of the residence time of carbon in the reservoir, τ , and the real discount rate, i, by substituting equations (3) and (4) into equation (5):

$$SP = \frac{\tau \cdot Ln[1+i]}{1+\tau \cdot Ln[1+i]} . \qquad (6)$$

Results for the sequestration potential as a function of time scale, τ , and discount rate, i, are presented in Figures 5 and 6.

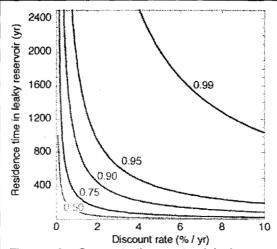


Figure 6. Sequestration potential for an idealized leaky reservoir as a function of discount rate and residence time. Residence time is related to the concept of a half-life of CO_2 in the leaky reservoir. (Half-life = 0.693 x residence time) For a discount rate of 5 % per year, sequestering CO_2 in a reservoir that leaks on the time scale of 100 yr saves approximately 80 % of the global warming cost of the CO_2 . For this discount rate, a reservoir that leaked on the 1000 yr time scale would save ~98 % of the global warming cost. Curves are calculated from equation (6).

Using results from the 1-D model

Ocean models do not, in general, allow analytic representations of their results. Nevertheless, equations (1) and (5) can be numerically integrated using fluxes predicted by the models. An example of these fluxes is represented in Figure 4. (These fluxes correspond to the carbon storage shown in Figure 3.) We used the box-diffusion model to calculate sequestration potential as a function of injection depth and discount rate. These results are plotted graphically in Figure 7.

Under the assumption of a constant cost of carbon emission and a 4 % discount rate, injecting only 900 m deep avoids ~90 % of the associated global warming costs; an injection 1700 m deep avoids > 99 % of the associated global warming costs. At a 6 % discount rate, an 750 m injection avoids > 90 % of the costs, whereas a 1400 m injection would avoid > 99 % of the costs.

Conclusions and Discussion

We have performed simulations of ocean carbon sequestration using one- and three dimensional ocean carbon cycle models. We find that the dimensional model results accord quite well with the three dimensional model results. Therefore, the one dimensional model is a tool of choice for exploring basic issues in direct oceanic CO₂ injection that do not depend on sitespecific or local characteristics of the injection. (For example, the 1-D model would not be appropriate for near field biotic impact studies.) Both one and three dimensional model results suggest that > 75 % of carbon injected at 3000 m depth is sequestered in the oceans for > 500 years.

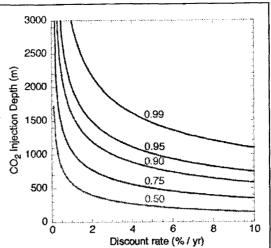


Figure 7. Sequestration potential for direct CO_2 injection as a function of discount rate and CO_2 injection depth, as calculated by the one-dimensional box-diffusion model. A 2000 m injection at a 3 % discount rate would avoid over 99 % of associated global warming cost, assuming constant carbon emission cost.

When CO₂ is sequestered in the oceans via direct injection, some of the CO₂ leaks out to the atmosphere and is then reabsorbed by the oceans. Our analysis of the problems suggests that this reabsorption should be considered part of the natural oceanic uptake of anthropogenic CO₂ and should not be credited towards ocean carbon sequestration.

We have defined measures of global warming cost, *GWC*, and the percentage of global warming cost avoided by sequestration, denoted sequestration potential, *SP*, and applied these measures to an idealized leaky carbon sequestration reservoir and the oceans.

Our analysis suggests that CO₂ injections into mid-depth waters may be an effective sequestration strategy, and injection into the deepest waters may not be economically justifiable. This conclusion could change if carbon emission costs were to rise rapidly in the

future. We find that ~98 % of global warming costs, GWC, can be avoided by CO₂ injection at ~1400 m with a 4 % discount rate, if the costs of carbon emission are taken to be constant in time. Under these same assumptions, it would take injection at ~1600 m to avoid ~99 % of the cost. The question of whether it makes sense to inject ~200 m deeper to avoid an additional 1 % of the global warming cost is largely an economic one. A fuller economic analysis would, of course, need to bring into consideration direct and indirect costs associated with implementing carbon sequestration strategies, consider feedbacks between economic choices and carbon emission prices.

It may turn out that rational economic analysis counsels against deep injections that are retained in the oceans for a long time in favor of mid-depth injections that achieve a relatively high sequestration potential. The effectiveness of ocean carbon sequestration is more site-dependent for injections at shallow depths than it is for deep injection (Figure 2). Therefore, for relatively shallow injection depths, site evaluation will depend to a greater degree on understanding local site characteristics.

The issue of the appropriate discount rate to use in problems involving intergenerational transfer of environmental assets is difficult. Arguments can be made that the appropriate discount rate for such situations should be near zero. At a zero discount rate with constant cost for carbon emission, there is no advantage to ocean carbon sequestration. Nevertheless, environmental costs can change with time, and it may prove useful to push carbon emissions to the distant future to slow near-term rates of climate change. In this

case, ocean carbon sequestration could prove useful even at zero discount rate. Nevertheless, with constant carbon emissions costs, even modest discount rates (e.g., 3 %) allow mid-depth oceanic injections of CO₂ to avoid the vast majority of global warming costs (Figure 7).

Most the carbon we emit into the atmosphere will end up residing in the ocean eventually. Ocean sequestration places the carbon there immediately, thus bypassing the atmosphere where CO₂ may have adverse impacts on climate as well as on the biota living in the ocean surface.

However, ocean carbon sequestration will only be acceptable if it can be shown that it is environmentally and economically preferable to alternative courses of action. Ocean sequestration is not the entire answer to the energy/climate/carbon problem, but it may be part of the answer, especially for coastally located CO₂ point sources far from acceptable geologic reservoirs.

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LITERATURE CITED

- Adams E. and Herzog H (1996) Environmental impacts of ocean disposal of CO₂, Finals Report, DOE Grant No. DE-FG22-94PC227, MIT Energy Lab, Cambridge, MA, USA.
- Adams E., Caulfield, J., Herzog H.J., and Auerbach, D.I. (1997) Impacts of reduce pH from ocean CO₂ disposal: Sensitivity of zooplankton mortality to model parameters, Waste Management (17) 375-380.
- Auerbach, D.I., J.A. Caulfield, E.E. Adams, and H.J. Herzog (1997) "Impacts of Ocean CO₂ Disposal on Marine Life: I. a toxicological assessment integrating constant- concentration laboratory assay data with variable-concentration field exposure," Environmental Modeling and Assessment, 2, pp. 333-343.
- Bacastow, R.B., Dewey, R.K., and Stegen, G.R. (1997) Effectiveness of CO₂ sequestration in the pre- and post-industrial oceans, Waste Mgmt (17) 315–322.
- Brewer, PG; Friederich, C; Peltzer, ET; Orr, FM. (1999) Direct experiments on the ocean disposal of fossil fuel CO₂. Science, V284, 943-945.
- Brewer, PG; Peltzer, ET; Friederich, G; Aya, I; and others (2000) Experiments on the ocean sequestration of fossil fuel CO2: pH measurements and hydrate formation. Marine Chemistry, V72 83-93.
- Broecker, W. S., Peng, T.-H., Ostlund, H. G., and Stuiver, M. (1985) The distribution of bomb radiocarbon in the ocean, J. Geophys. Res., 90, 6925–6939.
- Broecker, W. S., Sutherland, S., Smithie, W., Peng, T.-H., and Ostlund, G. (1995) Oceanic radiocarbon: separation of the bomb and natural components, Glob. Biogeochem. Cycles, 9, 263–288.
- Caldeira, K., and G.H. Rau (2000) Accelerating carbonate dissolution to sequester carbon dioxide in the ocean: Geochemical implications, Geophysical Research Letters, 27, 225–228.
- Caldeira, K., and P.B. Duffy (2000) The role of the Southern Ocean in uptake and storage of anthropogenic carbon dioxide, Science 287, 620-622.
- Caldeira, K., G.H. Rau, and P.B. Duffy (1998) Predicted net efflux of radiocarbon from the ocean and increase in atmospheric radiocarbon content, Geophysical Research Letters 25, 3811–3814.
- Caulfield, J.A., E.E. Adams, D.I. Auerbach, and H.J. Herzog (1997) "Impacts of Ocean CO₂ Disposal on Marine Life: II. probabilistic plume exposure model used with a time-varying dose-response model," Environmental Modeling and Assessment, 2, pp. 345-353.
- Cole, K.H., Stegen, G.R., and Spencer, D. (1993) The capacity of the deep oceans to absorb carbon dioxide, Energy Convers. Mgmt. (34) 991–998.
- De Baar, H.J.W. (1992) Options for enhancing the storage of carbon dioxide in the oceans: A review, Energy Convers. Mgmt. (33) 635-642.
- Dewey RK, GR Stegen and R Bacastow (1997) "Far-Field Impacts Associated With Ocean Disposal of CO₂," Energy Convers. Mgmt 38(Suppl.), pp. S349-S354.
- Dickson, A.E. (1990) Thermodynamics of the dissociation of boric acid in synthetic sea water from 273.15 to 298.15 K, Deep-Sea Research, 37, 755-766.
- Flannery, B.P., Kheshgi, H.S., Hoffert, M.I., and Lapenis, A.G. (1993) Assessing the effectiveness of marine CO₂ disposal, Energy Convers. Mgmt. (34) 983-989.
- Gent, P. R., and J. C. McWilliams (1990) Isopycnal mixing in ocean general circulation models, J. Phys. Oceanogr., 20, 150 155.

- Golomb D.S., Zemba, S.G., Dacey, J.W.H., and Michaels, A.F. (1992) The fate of CO₂ sequestrated in the deep ocean, Energy Convers. Mgmt. (33) 675–683.
- Golomb, D. (1993) Ocean disposal of CO₂: Feasibility, economics and effects, Energy Conver. Mgmt. (34) 967–976.
- Haugan, P.M., and Drange, H. (1992) Sequestration of CO₂ in the deep ocean by shallow injection, Nature (356) 318–320.
- Herzog, H.E., Adams, E., Auerbach, D., and Caulfield, J. (1995) Technology Assessment of CO₂ Ocean Disposal, Report MIT-EL 95-001, MIT Energy Lab, Cambridge, MA, USA.
- Herzog, H.J., Caldeira, K., and Adams, E. (in press) "Carbon Sequestration via Direct Injection", in Encyclopedia of Ocean Sciences (John Steele, steve Thorpe, and Karl Turekian, editors) Academic Press, Ltd, London.
- Hirai, S., Okazaki, K., Tabe, Y., and Hijikata, K. (1997) Numerical simulations for dissolution of liquid CO₂ droplets covered with clathrate film in intermediate depth of ocean, Energy Convers. Mgmt. (38) S313-S318.
- Hoffert, M.I., Caldeira, K, Jain, A.K., Haites, E.F., and others (1998) Energy implications of future stabilization of atmospheric CO₂ content, Nature (395) 881–884.
- Hoffert, M.I., Wey, Y.-C., Callegari, A.J., and Broecker, W.S. (1979) Atmospheric response to deep-sea injections of fossil-fuel carbon dioxide, Climatic Change (2) 53–68.
- Kheshgi, H.S., Flannery, B.P., Hoffert, M.I., and Lapenis, A.G. (1994) The effectiveness of marine CO₂ disposal, Energy (19) 967–975.
- Liro, C.R., Adams, E.E., and Herzog, H.J. (1992) Modeling the release of CO₂ in the deep ocean, Energy Convers. Mgmt (33) 667–674.
- Magnesen, T., and Wohl, T. (1993) Biological impact of deep sea disposal of carbon dioxide, Technical Report 77A, Bergen, Norway.
- Marchetti, C. (1977) On geoengineering and the CO₂ problem. Climatic Change (1) 59-68.
- Millero, F. J. (1995) The carbon dioxide system in the oceans, Geoch. Cosmch. Acta, 59, 661–677.
- Morishita, M., Cole, K.H., Stegen, G.R., and Shibuya, H. (1993) Dissolution and dispersion of a carbon dioxide jet in the deep ocean, Energy Convers. Mgmt. (34) 841–847.
- Nakashiki N, T Ohsumi and K Shitashima (1991) "Sequestering of CO₂ in a deep ocean -- fall velocity and dissolution rate of solid CO₂ in the ocean", CRIEPI Report (EU 91003), Japan.
- Nakashiki, N (1997) Lake-type storage concepts for CO₂ disposal option, Waste Mgmt. (17) 361–367.
- Nakashiki, N., and Ohsumi, T. (1997) Dispersion of CO2 injected into the ocean at the intermediate depth, Energy Convers. Mgmt. (38) 355-360.
- Oberhuber, J. M. (1993) Simulation of the Atlantic circulation with a coupled sea ice-mixed layer-isopycnal general circulation model. Part I: model description, J. Phys. Oceanogr., 23, 808-829.
- Oeschger, H., U. Siegenthaler, U. Schotterer, A. Gugelmann (1975) A box diffusion model to study the carbon dioxide exchange in natureTellus, 27, 168–192.
- Ohsumi T. (1995) CO₂ Disposal Options in the Deep Sea", Marine Technology Society Journal (29) 58-66.
- Ohsumi, T., Nakashiki, N., Shitashima, K., and Hirama, K. (1992) Density change of water due to dissolution of carbon dioxide and near-field behavior of CO₂ from a source on deep-sea floor, Energy Convers. Mgmt. (33), 685–690.

- Ozaki M., Sonada K., Fujioka Y., Tsukamoto O. and Komatsu M. (1995) 'Sending CO2 into deep ocean with a hanging pipe from afloating platform' Energy Convers. Mgmt. 36: 475-478.
- Pacanowski, R., K. Dixon and A. Rosati (1991), The G.F.D.L Modular Ocean Model Users Guide version 1, GFDL Ocean Group Technical Report No. 2, NOAA/Geophysical Fluid Dynamics Laboratory, Princeton, NJ.
- Rau, G.H., and Caldeira, K. (1999) Enhanced carbonate dissolution: A means of sequestering waste CO₂ as ocean bicarbonate. Energy Conversion and Management 40, 1803–1813.
- Reilly, J. (2001) Comparing A Forest Sequestration Plan with a Fossil Fuel Power Plant Plan, unpublished manuscript (jreilly@mit.edu).
- Roy, R. N., L. N. Roy, M. Vogel, C. P. Moore, T. Pearson, C. E. Good, F. J. Millero, and D. J. Cambell (1993) Determination of the ionization constants of carbonic acid in seawater, Mar. Chem., 44, 249-268.
- Shirayama, Y. (1998) Biodiversity and biological impact of ocean disposal of carbon dioxide, Waste Management (17) 381–384.
- Siegenthaler, U. (1983) Uptake of excess CO₂ by an outcrop-diffusion model of the ocean, J. Geophys. Res., 27, 3599–3608.
- Spencer, D.F., and North, W.J. (1997) Ocean systems for managing the global carbon cycle, Energy Convers. Mgmt. 38, S265–S271.
- Stegen, G.R., Cole, K.H., and Bacastow, R. (1993) The influence of discharge depth and location on the sequestration of carbon dioxide, Energy Convers. Mgmt. (34) 857–864.
- Stumm, W., and J.J. Morgan (1981) Aquatic Chemistry, 2nd ed., Wiley-Interscience, New York.
- Takeuchi, K., Fujioka, Y., Kawasaki, Y., and Shirayama (1997) Impacts of high concentrations of CO₂ on marine organisms: a modification of CO₂ ocean sequestration, Energy Convers. Mgmt. 38, S367–S372.
- Tamburri, MN; Peltzer, ET; Friederich, GE; Aya, I; and others (2000) A field study of the effects of CO₂ ocean disposal on mobile deep-sea animals. Marine Chemistry, V72, 95-101.
- Teng, H., Yamasaki, A., and Shindo, Y.. (1997) Influence of disposal depth on the size of CO₂ droplets produced from a circular orifice, Energy Convers. Mgmt. 38, S325–S329.
- Thorkildsen, F, Alendal, G. (1997) LES study of flow around a CO₂-droplet plume in the ocean. Energy Conversion and Mgmt. (38) S361–366.
- Weiss, R.F. (1974) Carbon dioxide in water and seawater: the solubility of a non-ideal gas, Marine Chemistry, 2, 203–215.
- Wilson, T.R.S. (1992) The deep ocean disposal of carbon dioxide, Energy Conver. Mgmt. (33) 627–633.
- Wong, C.S., and Mattear, R. (1993) The storage of anthropogenic carbon dioxide in the ocean, Energy Convers. Mgmt. (34) 873–880.
- Xu, Y., Ishizaka, J., and Aoki, S. (1999) Simulations of the distributions of sequestered CO₂ in the North Pacific using a regional general circulation model, Energy Convers. Mgmt. (40) 683–691.